Notes: Chapter 23

Wednesday, January 10, 2007
12:04 AM

Chapter 23: The Transition Elements and Their Coordination Compounds

Homework:

The transition elements (B group elements) as a group are colorful, useful and fascinating. Many of their properties are due to the filling of d-orbitals and f-orbitals, and an understanding of the electronic configuration is essential. You may need to review the electron configuration for these elements in your text.

Problem:

Determine the possible charge states for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn.

General Trends

Atomic radius decreases as you go across the periodic table toward the middle of the transition elements, and then increase from the middle to the end of the transition series. Period 4 transition elements are significantly smaller than period 5 and period 6 transition elements. Period 5 and period 6 transition elements are virtually the same size due to an effect called the lanthanide contraction which is caused by a substantial increase of nuclear charge since the lanthanide f-block elements are filled before completing the d-block. Chemical properties parallel the covalent radii similarities for the period 5 and 6 transition elements.

The ionization energy generally increases across the transition series. Period 4 and 5 transition elements have similar ionization energies; however period 6 transition elements have significantly higher ionization energies making them less reactive than period 4 and 5.

Oxidation states of the transition elements are variable. You should know the possible charge states for these elements. As the oxidation state of the transition element increases the covalent nature of the bond increases. Consider the following problem.

Problem:

Which compound has a higher melting point, $TiCl_2$ or $TiCl_4$? Why?

Demo:

Chromate-dichromate acid equilibrium.

Demo:

Complex ion formation of several transition elements.

Complex Ions and Coordination Compounds

Complex ions are formed when ligands bond to a central metal ion. A ligand is a Lewis base and donates a pair of electrons to the metal. The number of ligands a metal can accept is called the coordination number.

Problem:

What is the coordination number for the following substances?

$Na_3Fe(CN)_6$, $CaCu(NH_3)_4$, $K_2Ni(H_2O)_4(NH_3)_2$, $Ag(NH_3)_2^+$

Many Lewis bases can act as ligands; NH_3, H_2O, halogens, CO, CN^-, and OH^- to name just a few. All of these ligands can donate 2 electrons to a metal ion and are called monodentates. Bidentate ligands can donate two pairs of electrons to the central metal atom, and polydentate ligands can donate more than two pairs of electrons.

Bidentates: Ethylenediamine (en), oxalate (ox)

Polydentates: ethylene diamine tetra acetate (EDTA), heme (see pages 1006-1007)

Complexes of metal ions by polydentates are sometimes called chelates and the polydentates are called chelating agents.

NOTE: The word dentate means tooth and the word chelate means claw or pincer.

Complex Ion Nomenclature

1) Positive ions named first.
2) When naming the complex, ligands are named first in alphabetical order not including Greek prefixes.
3) a) Anion ligands end in -o.
    b) Neutral ligands are usually given the name of the molecule with the following exceptions; NH_3 ammine, CO carbonly, and H_2O aqua.
    c) Greek prefixes indicate the number of a type of ligand present in a complex. di, tri, tetra, penta, hexa
    d) When the name of a ligand contains a Greek prefix, an alternate numbering system is used. bis, tris, tetrakis, pentakis, hexakis
4 The name of the central metal atoms comes last. If the complex is an anion the Latin name is given and ends in -ate followed by the oxidation state in Roman numerals. If the complex is neutral or positive, the English name is given followed by the oxidation state in Roman numerals.

Problem:

Name the following substances.

$Ca_2Fe(CN)_6$
$[Fe(NH_3)_3H_2OCl_2]Cl$
$Fe_2[Ni(C_2O_4)_2]_3$
$[Pt(NH_3)_4ClBr]I_2$

$[Cr(H_2O)_6]Cl_3$
$[Cr(H_2O)_5Cl]Cl_2•H_2O$
$[Cr(H_2O)_4Cl_2]Cl•2H_2O$

Structure and Isomerism in Coordination Compounds

Isomerism = same molecular formula with different structure.

Structural Isomerism

Stereoisomers = isomers having same formula and bonded in the same order, but different in spatial arrangement.

I.e.) 1,2 dichloroethene

Ionization isomers = isomers having same formula, but differing in charge state of central atom because of different coordination.

I.e.) $[Co(NH_3)_5SO_4]Br$ & $[Co(NH_3)_5Br]SO_4$

Hydrate isomers = isomers having same formula, but different number of water in coordination sphere. I.e.) $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2•H_2O$, $[Cr(H_2O)_4Cl_2]Cl•2H_2O$

Coordination isomers = isomers having same formula but different atoms coordinated to anion complex and cation complex.

I.e.) $[Cu(NH_3)_4][PtCl_4]$, $[CuCl_4][Pt(NH_3)_4]$

Linkage isomers = isomers where ligands use different atoms to bond to central metal ion. I.e.) SCN or NCS, NO_2, or ONO, (Ambidentate ligands)

Geometric isomers= isomers where atoms are bonded to one another in the same way, but in different relative orientation = stereoisomers.

I.e. cis-dibromodichloroplatinate (IV) and
trans-dibromodichloroplatinate (IV)

Optical isomers = isomers having nonsuperimposible mirror images. Only molecules having no plane of symmetry can have optical isomers. I.e.) dibromobisethylenediaminecobalt (IV). Optical isomers have the unusual property of rotating a plane of polarized light. If the plane of light is rotated to the right (clockwise) the substance is called dextrorotatory (d), if the plane of light is rotated to the left (counterclockwise) the substance is called levorotatory (l). The physical and chemical properties of the two isomers are identical. A mixture of equal parts d and l gives a racemic mixture which does not rotate a plane of polarized light.

Valence Bond Theory of Complexes

Paramagnetism = substances with unpaired electrons attracted into a magnetic field.

Diamagnetism = substance with all electrons paired.

Ligands attach themselves by donating electron pairs to the central metal atom. Two classes of compounds can form when ligands bond to metals; high spin or low spin depending on the nature of the ligands. More on the nature of the ligands will be explained in the crystal field theory. Consider the following complexes of nickel II.

Problem:

Hexaaquanickel (II) ion is paramagnetic where hexacyanonickelate (II) is diamagnetic.

a) Explain this in terms of VBT orbital diagrams.
b) What is the hybridization of these two complexes?
c) Which one is high spin and which one is low spin?

Extra credit:

In some chemical text or other chemistry resource there is a name given to the magnetic phenomenon related to the number of unpaired electrons. I.e.) Three ______________ units are due to three unpaired electrons. What the blank are they?

Nickel (II), palladium (II) and platinum (II) commonly form square planar complexes commonly form square planar complexes (dsp^2). Nickel can also form tetrahedral complexes (sp^3).

Problem:

Tetracyanonickelate (II) is a low spin complex where tetraamminenickel (II) is high spin. What is the shape of each complex?

Crystal Field Theory

Crystal field theory gives us the answer to the question "Why does a high spin or low spin complex form for a particular ligand-metal complex?". The theory argues that the d-orbitals split as a result of the electric field (crystal field) imposed on them by the ligands. Initially all d-orbitals are at the same energy. Consider the d-orbitals (See page 1022) and what might happen to the energy of these orbitals as six ligands approach along the ±x, ±y and ±z axes. As the ligands move closed to the d-orbital set, they interact in a head-on fashion with the d_z2 and the $d_x2\text{-}_y2$ orbitals. Direct interaction raises the energy of these orbitals. The ligands will be directed between the lobes of the d_{xy}, d_{xz}, and the d_{yz}. When ligands are between the lobes of orbitals, the energy is lowered for these orbitals.

______ ______
d_z2 $d_{x2\text{-}y2}$

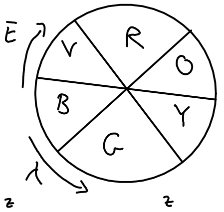
______ ______ ______ ______ ______ D =

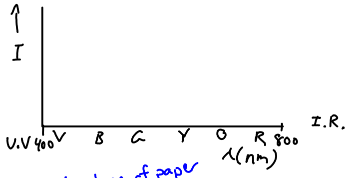
Energy difference

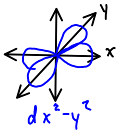
______ ______ ______
d_{xy} d_{xz} d_{yz}

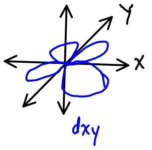
Orbital energy **without** ligand field. Orbital energy **with** ligand field .

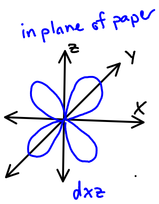
The size of the energy difference between the lower and higher d-levels is called D (delta). This energy difference is directly related to the ability of the ligand to apply an electric field to the d-orbitals of the

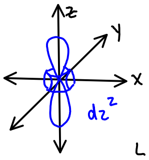


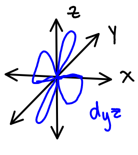




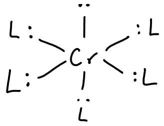








metal ion. Ligands that bond strongly to the metal impose a stronger field than those ligands that bond weakly to the metal. A list of ligands called the spectrochemical series gives the relative ability of ligands to bond (apply a field) to the metal ion.



The Spectrochemical Series

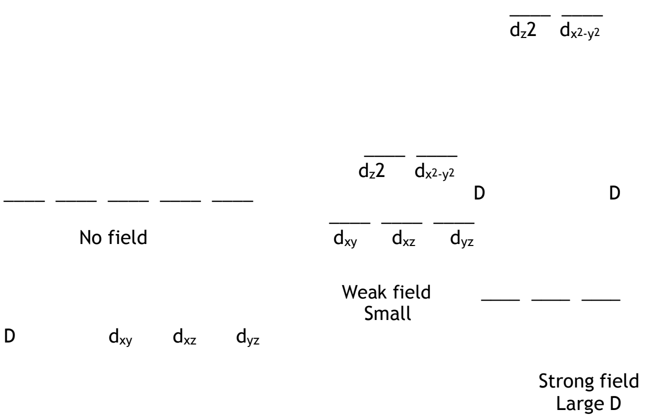
Weak field ligands — Strong field ligands

$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< NO^- < CN^- < CO$

High spin complexes — Low spin complexes

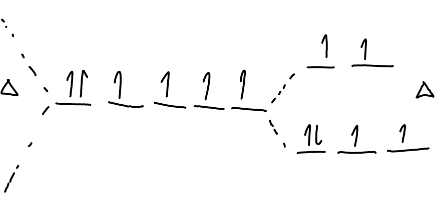
Δ< Pairing energy — Δ> Pairing Energy

The magnitude of D determines the magnetic properties (high spin or low spin) of a complex .



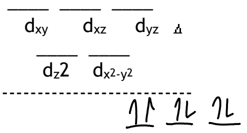
Problem:

How many unpaired electrons will $Fe(CN)_6^{3-}$ and $Fe(Cl)_6^{3-}$ have? Use the above energy diagram. 0 4

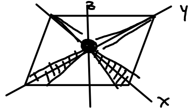


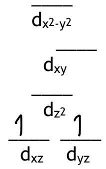
For tetrahedral complexes the energy diagram is:

↳Always high spin



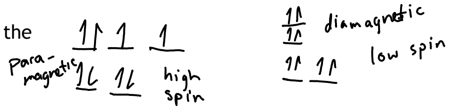
For square planar complexes the energy diagram is:





Problem:

$Ni(CN)_4^{-2}$ is diamagnetic and $Ni(NH_3)_4^{+2}$ is paramagnetic. Describe the electron distribution in terms of crystal field theory.



Visible Spectra of Transition-Metal Complexes

The color of a complex is due to the absorption of frequencies of light that correspond to the difference in energy between d-orbital energy levels. The colors not absorbed by the complexes are the colors we see.

Problem:

$Fe(CN)_6^{3-}$ absorbs light having wavelengths less than 620 nm. What is the color of the complex? See page 1027

Problem:

$Ti(H_2O)^{3+}$ absorbs light having wavelengths from 450 to 620 nm. What is the color of the complex? See page 1027

Problem:

A complex absorbs light having wavelengths less than 500 nm and more than 560 nm. What is the color of the complex? See page 1027

Problem:

$Cu(H_2O)^{2+}$ absorbs light most strongly at 590 nm. What is the value of D in kJ/mol.

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